

PROCESS FOR THE PREPARATION OF POLY(SILYL ESTER)S,
AND THEIR USES

The present invention relates to a new method for the
5 preparation of poly(silyl ester)s. The invention further
relates to novel poly(silyl ester)s, and in another
aspect, the invention further relates to the use of
hydrolysable poly(silyl ester)s where the use of
hydrolysable silyl ester groups is advantageous.

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Poly(silyl ester)s possess a variable yet predictable
degradation behaviour and as such, have a broad range of
potential applications wherever the presence of
hydrolysable groups is advantageous. For instance, it is
15 known to use degradable polymers in general in the
medical, environmental, biomedical, and agricultural
areas, wherein the ability of the polymers to break down
into biologically or environmentally resorbable small-
molecule byproducts is of great use. WO 03/105920
20 discloses the use of polymer containing coating
compositions for medical implant devices. Poly(silyl
ester) compositions are believed by the present inventors
to represent viable alternatives to the compositions
disclosed therein.

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Another application is as a resin or co-resin for self-
polishing antifouling paints, for instance, as binders for
modern antifouling coatings, although the use of
hydrolysable poly(silyl ester)s, as noted above, will have
30 many applications where the fact that the degradation
behaviour can be affected by the nature of the
functionality attached to the silicon atoms would be a
positive advantage.

CONFIRMATION COPY

Trialkylsilylcarboxylates of aliphatic carboxylic acids can be obtained by transesterification. H.H. Anderson et al describe in J.Org.Chem 1716 (1953) the reactions of triethyl silyl acetates and diethyl silyl diacetates with halogenated propionic acids and in J.Org.Chem. 1296 (1954) the reactions of dimethylsilyl di(trifluoro acetate) or dimethylsilyl dipropionate with chloroacetic acid; they distill the acetic, propionic or trifluoroacetic acid under reduced pressure.

Russian chemists (Izv.Akad.Nauk.Ussr.Ser.Khim. 968 (1957)) run similar reactions but at much higher temperatures (190-210°C).

JP 95070152 A discloses reactions of trialkylsilylacetates with C6 to C30 carboxylic acids (e.g. palmitic, myristic, benzoic,...); the acetic acid is distilled under reduced pressure or azeotropically with hexane.

Poly(silyl ester)s are characterised by the fact that they comprise more than one silyl carboxylate unit in the oligomeric/polymeric backbone. In other words, poly(silyl ester)s contain -Si-O-C(O)- linkages along the polymer backbone, and are a class of degradable polymer systems with a variable, yet predictable, degradation behaviour.

Silyl ester functionalities have been prepared by many routes and therefore it may have been envisaged that the synthesis of poly(silyl ester)s would be relatively straightforward. However, problems such as salt formation, side reactions, monomer insolubility/impurity, and/or incomplete reaction, ensured that many of the

envisaged polymer syntheses were not in fact suitable. Indeed, it is only recently that the incorporation of acyloxysilane groups in a polymer backbone has actually been achieved.

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Wooley et al have developed and disclosed synthetic routes for the preparation of poly(silyl ester)s, including transsilylation esterification of AA/BB comonomers (see Macromolecules (1995) 28 8887; Macromolecules (1998) 31 7606; J.Polym.Sci., Part A : Polym.Chem. (1999) 37 3606; 10 Macromolecules (1998) 31 15; and J.Organomet.Chem. (1998) 542 235), transsilylation esterification of AB monomers (see Macromolecules (2000) 33 734; and J.Organomet.Chem. (1998) 542 235), hydrosilylation of AB monomers (see 15 Macromolecules (2000) 33 734), and cross-dehydrocoupling polymerisation of AB and AB₂ monomers (see Macromolecules (2001) 34 3215, and references cited therein).

For example, the transilylation ester interchange reaction 20 of chlorosilanes with TMS-blocked silyl esters at temperatures in the range of 100-135°C for 10-14 days, leading to the formation of corresponding polymers with the concomitant distillation of trimethylsilyl chloride, using, for example, N,N-dimethylformamide (DMF) as a 25 catalyst, has been described by Wooley et al, in Macromolecules (1998) 31 15. This method does have its advantages; no base is required, and the trimethylsilyl chloride by-product is volatile. Moreover, the reaction proceeds at relatively low temperatures, and without the 30 addition of a solvent. However, TMS-blocked silyl esters are expensive reagents and the release of trimethylsilyl chloride is harmful to the environment.

Another method described by Wooley et al in Macromolecules (2000) 33 734 and Macromolecules (2001) 34 3215 is the polymerisation accomplished via hydrosilylation between a silyl hydride function and a carbon/carbon double bond or
5 a carboxylic acid function present in the same molecule (AB monomer system) or in different molecules (AA/BB monomer system). This method suffers from the disadvantages of requiring the use of transition metal catalysts such as platinum or palladium derivatives
10 (Pt(COD)Cl₂; Pd/C) in order to generate hydrogen when carboxylic acid functions are involved and the limited accessibility of the starting materials.

Therefore, there remains the need to find a novel method
15 for the preparation of poly(silyl ester)s avoiding or at least alleviating the aforementioned problems associated with the prior art methods of synthesising hydrolysable poly(silyl ester)s.

20 Therefore, an object of the present invention is to provide a novel process capable of readily preparing poly(silyl ester)s in a high yield from easily and readily available starting materials.

25 Another object of the present invention is to provide a more efficient process for the preparation of poly(silyl ester)s compared to those previously disclosed methods discussed above.

30 A further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s which proceeds at an acceptable rate even without the presence of any added catalyst.

A yet further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s wherein only harmless and easily distillable molecules are released.

A yet still further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s wherein the degree of conversion of the starting materials to the target product may be monitored by conventional analytical tools and/or by determining the amount of distilled molecules released.

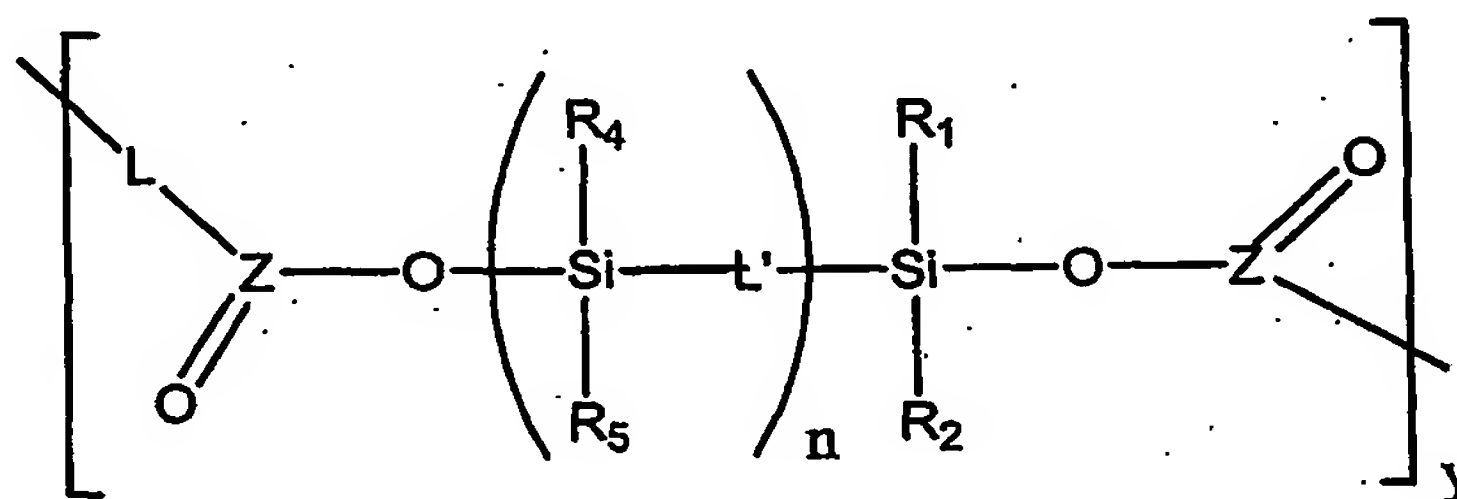
Thus, overall, the object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s offering some improvement *vis-à-vis* the disadvantages disclosed hereinbefore.

The present invention is based on the reaction of polyacids (and by "polyacids" we mean an organic moiety comprising at least two acid groups; for example at least two carboxylic, sulphuric, phosphoric, and the like, acid groups; preferably, we mean polycarboxylic acids) with polyacyloxy silyl derivatives to synthesise poly(silyl ester)s by silyl ester transesterification. The use of polyacids and the technique of transesterification in the synthesis of poly(silyl ester)s was unexpected as hitherto, the technique of transesterification had only been used to synthesise organosilylated carboxylate monomers, and previously disclosed methods of synthesising poly(silyl ester)s were either found to be ineffective at polymer formation or used expensive reactants and/or produced harmful by-products and/or required an added

catalyst and/or could not be followed easily by conventional analytic tools.

The present inventors have surprisingly found that by reacting polyacids with polyacyloxysilyl derivatives, poly(silyl ester)s could be synthesised.

According to a first aspect, the present invention relates to a new process for the preparation of poly(silyl ester)s comprising a structural unit of the formula (I)



(I)

wherein each R_4 and R_5 may be hydroxyl or may be independently selected from hydrogen, alkyl, cycloalkyl, aryl, alkoxyl, aryloxy, $-\text{L}'-\text{SiR}_1\text{R}_2-$, $-\text{L}'-\text{SiR}_4\text{R}_5\text{R}_{10}$, $-\text{L}'-(\text{SiR}_4\text{R}_5\text{L}')_n-\text{SiR}_1\text{R}_2-$, alkenyl, alkynyl, aralkyl or aralkyloxyl radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, hydroxyl, aryl, aryloxy, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R_4 or R_5 may independently be an $-\text{O}-\text{Z}(\text{O})-\text{L}-$ group, where R_{10} is defined as is R_7 below,

wherein each R_1 and R_2 may independently represent hydrogen, hydroxyl, alkyl, cycloalkyl, alkenyl, alkynyl,

alkoxyl, $-L'-SiR_4R_5R_{10}$, aryl, aryloxy, aralkyl or
aralkyloxy radical optionally substituted by one or more
substituents independently selected from the group
comprising alkyl, alkoxyl, aralkyl, aralkyloxy, aryl,
5 aryloxy, halogen, hydroxyl, amino (preferably, tertiary
amino) or amino alkyl radicals, or R_1 or R_2 may
independently be an $-O-Z(O)-L-$ group,

wherein L represents a hydrocarbyl or substituted
10 hydrocarbyl group, wherein said substituted hydrocarbyl is
substituted by one or more substituents independently
selected from the group comprising alkyl, cycloalkyl,
carboxyl, substituted carboxyl, alkoxyl, aralkyl,
aralkyloxy, aryl, aryloxy, hydroxyl, halogen, amino or
15 amino alkyl radicals, or a polymer with pendant acid
groups,

L' represents O , S , or NR_6 , $L-(NR_6-L)_p$ (where $p = 1$ to 10),
where R_6 is defined as is R_7 below, or L ,

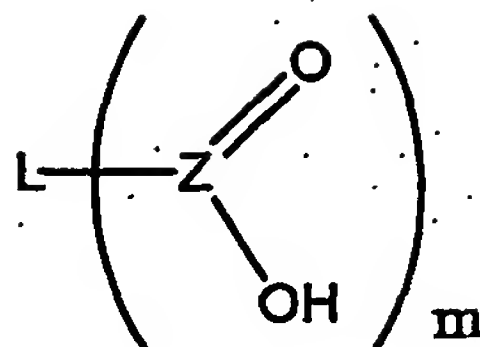
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each n independently represents a number of $-Si(R_4)(R_5)-$
 $L'-$ groups from 0 to 1000,

and y represents a number of silyl ester repeat units from
25 2 to 100000, more preferably 2 to 10000, most preferably 2
to 1000,

which process comprises the step of reacting;

a polyacid of formula (II)



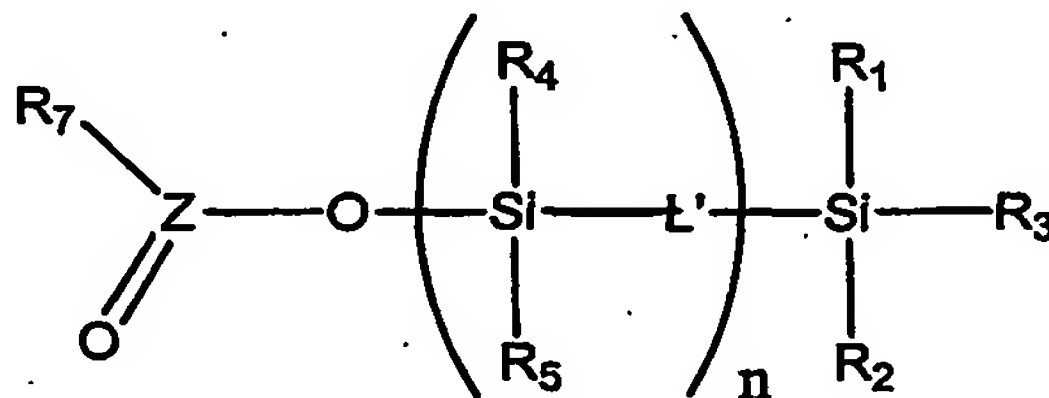
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(II)

wherein Z(O)OH represents the acid moiety attached to L, m is an integer from 2 to 100000, preferably 2, and L is as defined above,

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with a polyacyloxysilyl derivative of formula (III)



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(III)

wherein R₁, R₂, R₄, R₅, L' and n are as defined above, except R₁, R₂, R₄ and R₅ in (III) are -O-Z(O)-R₈, where R₈ is defined as is R₇ below, when the equivalent group in (I) is -O-Z(O)-L-, and R₇ is a hydrogen atom, an aralkyl, aryl, alkenyl, alkynyl, or alkyl group optionally substituted with one or more substituents selected from the equivalent substituents as defined for R₁, R₂, R₄ and R₅ above,

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and R_3 is the group $-O-Z(O)-R_9$, where R_9 is defined as is R_7 above,

whilst removing the formed acid group(s) of formula (IV)
5 and (V) and (VI),

$R_7 Z(O)OH$ (IV),

$R_9 Z(O)OH$ (V),

10 $R_8 Z(O)OH$ (VI),
from the system.

Essentially, it is required that the polyacyloxysilyl derivative is such that there is more than one acyloxy
15 group attached to one or several silicon atoms. Moreover, when $n=0$ there are a maximum of four acyloxy groups on the silicon atom; and when $n>0$, the terminal silica atoms have a maximum of three acyloxy groups and the non-terminal silicon atoms a maximum of two acyloxy groups.

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Suitably, the poly(silyl ester)s comprising a structural unit of formula (I) will terminate with the groups $-SiR_1R_2R_3$ and $-O-Z(O)-R_7$.

25 In cases wherein m is greater than 2, i.e. in cases where the polyacid contains more than 2 $(Z(O)OH)$ groups, then L in formula (I) will have attached thereto the $(Z(O)OH)$ groups in excess of 2, pendant acid groups, and therefore polymerisation with the polyacyloxysilyl derivative can
30 further occur from this/these additional $(Z(O)OH)$ sites.

Preferably, wherein R^1 , R^2 , R^4 and R^5 are alkoxyl, aryloxyl, alkaryloxyl or hydroxyl in formula (III), they may represent $-O-Z(O)-L-$ in formula (I).

5 Preferably, R_4 and R_5 each independently represent an alkyl, an alkoxyl, an aryl, an hydroxyl group or an $-L'-(SiR_4R_5L')_n-SiR_1R_2-$ group, wherein L' , R_1 , R_2 , R_4 and R_5 are as defined above and wherein preferably, $n=0-100$ and more preferably, $n=0-10$, most preferably $n=0$ but is also
10 possibly 1, 2, 3, 4 or 5, preferably 1.

More preferably, R_4 and R_5 in formula (III) are each independently selected from the group comprising an alkyl group, an hydroxyl group, an alkoxyl group or an $-L'-(SiR_4R_5L')_n-SiR_1R_2-$ group, wherein L' , R_1 , R_2 , R_4 and R_5 are
15 as defined above. Most preferably, R_1 , R_2 , R_4 and R_5 each independently represent an alkyl group. The said alkyl groups may be branched or linear.

20 Preferably L' represents O.

Preferably Z represents C, POH, P or S=O, more preferably, C. For example, each Z in formula (II) or (III) may preferably independently represent C, POH, P or S=O, more
25 preferably, C. For the avoidance of any doubt, when Z is not C, the term polyacyloxysilyl is to be construed/amended accordingly.

According to an embodiment of the present invention, R_1 ,
30 R_2 , R_4 , R_5 and R_8 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl, phenyl, and vinyl. Preferably R_1 , R_2 , R_4 and R_5 are selected from the group

consisting of methyl, ethyl, isopropyl, phenyl, and vinyl.
More preferably, R_1 , R_2 , R_4 , R_5 and R_8 are methyl.

Preferably, the groups R_1 and R_2 are the same. Equally
5 preferably, the groups R_7 and R_9 are the same, more
preferably an alkyl group, most preferably methyl.

Preferably, R_7 and R_9 each represent an alkyl group, more
preferably methyl.

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Preferably, R_6 is alkyl, most preferably methyl.

When R_4 and R_5 are alkoxy, they are preferably C_1 - C_8 oxyl
groups which may be branched or linear, more preferably,
15 C_1 - C_4 oxyl groups, most preferably, a methoxyl group.

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Preferably, when R_4 or R_5 is selected as $-L'-(SiR_4R_5L')_n-$
 SiR_1R_2- , the R_4 and R_5 groups attached to the silicon
radical in the selected group are not themselves,
20 $-L'-(SiR_4R_5L')_n-SiR_1R_2-$.

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Preferably, n as used herein each independently represent
0 to 500, more preferably 0 to 100, most preferably 0 to
10. Especially preferred values for n are selected from
0, 1, 2, 3, 4 or 5, most especially from 0 and 1.

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The process of the invention enables one to obtain
poly(silyl ester)s by reacting polyacids, preferably
polycarboxylic acids, with polyacyloxysilyl derivatives.

The present invention relates to a new process for the
synthesis of poly(silyl ester)s according to the general
scheme whereby a polyacyloxysilyl derivative of formula

(III), is reacted with a polyacid, preferably a polycarboxylic acid, of formula (II) and comprising at least two acid groups, preferably two carboxylic acid groups, to form poly(silyl ester)s comprising a structural unit of formula (I).

The reactants are mixed together either with or without solvents. Preferably, the reaction is carried out in a suitable solvent. Suitable solvents which can be used in the process of the invention include non polar inert solvents, cyclic and non-cyclic aliphatic hydrocarbons, cyclic and non-cyclic ethers, esters, and the like. Examples of suitable solvents which can be used in the process according to the invention include pentane, cyclopentane, hexane, cyclohexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthalene, diethyl ether, diisopropyl ether, diisobutyl ether, N,N-dimethylformamide, N-methylpyrrolidone, N,N-dimethylacetamide, and the like and mixtures thereof.

Preferred solvents are those which cause no distillation of any of the reactants, especially those solvents which allow preferential distillation of one of the products. Thus, a more especially preferred solvent is a solvent which forms a low boiling azeotrope with the distilled acid product of the process of the invention. Still more especially preferred solvents are those which form a heterogeneous low boiling azeotrope with the distilled acid product.

More preferably, the solvents are independently selected from pentane, hexane, cyclohexane, heptane, toluene and xylene.

- 5 Preferably, the temperature of the reaction depends on the boiling point of the acid or its azeotrope that has to be distilled, the shape of the reactor and the height of the distillation column.
- 10 Typically, the reaction is carried out in the range 0°C - 200°C, more preferably, 60-190°C, most preferably, 110-180°C.

15 Preferably, the molar ratio of the reactive groups present in the polyacyloxysilyl derivative and the polyacid is between 1:100 and 100:1, more preferably between 10:1 and 1:10, most preferably, between 2:1 and 1:2. Preferably, the molar ratio of acyloxy group:acid group is approximately 1:1.

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Preferably, the solvent, where present, is at least 10 wt% of the total reaction mix at the start of the reaction, more preferably, at least 20 wt%, most preferably, at least 30 wt%. The reaction may be carried out at
25 atmospheric pressure although both higher and lower pressures are also possible.

The reaction may also be performed without solvent and accordingly suitable ranges of solvent are 0-99 wt% of the
30 total reaction mix, more preferably, 20-50 wt%, most preferably 30-40 wt%.

In a preferred embodiment, L represents or is derived from an alkyl, aryl, alkenyl, alkynyl, or aralkyl radical, or may represent a polymer, preferably comprising 1 to 10000 carbon atoms, more preferably 1 to 1000 carbon atoms, most preferably 1 to 100 carbon atoms.

In a further preferred embodiment, L represents $-(CH_2)_n-$, wherein n is an integer between 1 and 10, preferably between 2 and 8, more preferably between 4 and 6, most preferably 4, or in a further embodiment, L represents a lactic acid or rosin residue, for example the non-carboxylic acid portions, or portions minus two of the carboxylic acid groups present, of a polylactic or substituted polylactic acid, e.g. di-lactic acid, rosin and/or rosin derivatives, e.g. DYMEREX[®] (rosin dimer).

The reaction progress may be monitored by any suitable analytical method as well as with the determination of the amount of acid distilled.

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Although any dicarboxylic or, more generally, polycarboxylic acid, or even polyacid, of formula (II) may be used in the process according to the invention, dicarboxylic acids are preferred, and preferred examples of dicarboxylic acids are adipic acid, oxalic acid, succinic acid, glutaric acid, phthalic or isophthalic or terephthalic acids, and the like, a polylactic acid such as di-lactic acid, and rosinous dicarboxylic acids such as DYMEREX[®] (rosin dimer), or polymer thereof. Moreover, formula (II) may represent a polymeric polyacid.

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The polyacyloxysilyl derivatives which can be used in the process according to the invention are preferably those

derived from carboxylic acids having a boiling point of maximum 162°C, preferably of maximum 140°C, more preferably of maximum 120°C, in order to facilitate the removal of the product after the transesterification.

5 Examples of suitable carboxylic acids are formic acid, acetic acid, propionic acid and butyric acid. Formic acid and acetic acid with respectively 100°C and 118°C as boiling points are preferred, with acetic acid being particularly preferred.

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In another embodiment of the invention the polyacyloxysilyl derivatives are derived from partially or totally halogenated acids, preferably from fluorinated or chlorinated acids, more preferably from trifluoroacetic

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acid with 70°C as boiling point.

The polyacyloxysilyl derivatives for use in the process of the invention are known (see table) or can be obtained by known methods. Some non-limiting examples are given in

20

the following table:

polyacyloxysilyl derivative	CAS registry number
tetramethyl-1,3- diacetoxysiloxane	5314-58-9
dimethyldiacetoxysilane	2182-66-3
diethyldiacetoxysilane	18269-81-3
diphenyldiacetoxysilane	2565-07-3
vinylmethyldiacetoxysilane	2944-70-9
methyltriacetoxysilane	4253-34-3
ethyltriacetoxysilane	17689-77-9
vinyltriacetoxysilane	4130-08-9
phenyltriacetoxysilane	18042-54-1
tetraacetoxysilane	562-90-3
butanoic acid, 1,3,5-triethyl-1,3,5-tripropyl-1,5-trisiloxanediyl ester	34740-39-1
1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-,	

dipropionate	34732-57-5
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(7-hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxanoxy)-, diacetate	33002-43-6
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(5-hydroxy-1,1,3,3,5,5-hexamethyltrisiloxanoxy)-, diacetate	33002-42-5
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(3-hydroxy-1,1,3,3-tetramethyldisiloxanoxy)-, diacetate	33002-41-4
1,9-pentasiloxanediol, 1,3,5,7,9-pentamethyl-1,3,5,7,9-pentavinyl-, diacetate	23174-06-3
1,7-tetrasiloxanediol, 1,3,5,7-tetraethenyl-1,3,5,7-tetramethyl-, diacetate	23174-05-2
1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octaethyl-, diacetate	23174-10-9
1,5-trisiloxanediol, 1,3,5-triethenyl-1,3,5-trimethyl-, diacetate	23174-04-1
heptasiloxane, 1,1,1,13-tetraacetoxy-3,3,5,5,7,7,9,9,11,11,13,13-dodecamethyl	22306-76-9
1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-trimethyl-, diacetate	21982-13-8
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dibutyrate	21961-88-6
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dipropionate	21961-87-5
1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, diacetate	21961-86-4
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, diacetate	21961-85-3
1,1,1,7-tetrasiloxanetetrol, 3,3,5,5,7,7-hexamethyl-, triacetate	19363-46-3
1,5-trisiloxanediol, 1,1,3,5,5-pentamethyl-3-vinyl-, diacetate	18038-26-1
1-tetrasiloxanol, 7-acetyl-1,1,3,3,5,5,7,7-octamethyl-, acetate	6990-26-7
1-pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate; pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate	6904-56-9
1,9-pentasiloxanediol, decamethyl-, diacetate	5314-61-4
1,5-trisiloxanediol, hexamethyl-, diacetate	5314-59-0
1,17-nonasiloxanediol, octadecamethyl-, diacetate	3527-48-8
1,15-octasiloxanediol, hexadecamethyl-, diacetate	3454-14-6
1,7,13-heptasiloxanetriol, tridecamethyl-, triacetate	3293-05-8
1,1,7-tetrasiloxanetriol, 1,3,3,5,5,7,7-heptamethyl-, triacetate	3293-04-7
1,13-heptasiloxanediol, tetradecamethyl-, diacetate	3293-03-6
1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octamethyl-,	

diacetate	3293-02-5
ditert-butylldiacetotoxysilane	168153-12-6
ditert-butoxydiacetoxysilane	13170-23-5

Suitably, there is no limit on the molecular weight of the final product. However, the molecular weight is preferably in the range 1000 to 1000000 kD, more preferably 1000 to 100000 kD, most preferably 1000 to 10000 kD.

Drawdowns of resins obtained by the process of the invention may be dried at temperatures in the range 0-150°C, preferably 18-100°C, more preferably 19-35°C.

As used herein, the term "polymer" refers to the product of a polymerisation reaction, and is inclusive of homopolymers, copolymers, e.g. polysilanol, polyols, polyamines, etc. (which can react/esterify with the polyacid and/or polyacyloxysilanes; in the case of polysilanol, the non-hydrolysable Si-O bond will be part of the polymer), terpolymers, etc.

As used herein, the term "independently selected" or "independently represent" indicates that each radical, e.g. R, so described, can be identical or different.

The term "alkyl", as used herein and unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms more preferably 1 to 8 carbon atoms, still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Said radicals

may be substituted, i.e. optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of such radicals include and may be independently selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, iso-amyl, n-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl, and the like.

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The term "alkynyl", as used herein and unless otherwise defined, relates to hydrocarbon radicals having one or several triple bonds, having straight, branched, polycyclic or cyclic moieties or combinations thereof and having from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably from 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkynyl radicals include ethynyl, propynyl, (propargyl), butynyl, pentynyl, hexynyl and the like.

The term "aryl", as used herein and unless otherwise defined, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-

nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and the like.

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The term "alkenyl", as used herein and unless otherwise defined, relates to hydrocarbon radicals having one or several double bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Said radicals may be substituted, i.e. optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, 1-propenyl, 2-butenyl, 2-methyl-2-butenyl, isopenyl, farnesyl, geranyl, geranylgeranyl and the like.

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The term "aralkyl", as used herein and unless otherwise defined, relates to a group of the formula alkyl-aryl, in which alkyl and aryl have the same meaning as defined above. Said radicals may be substituted, i.e. optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aralkyl radicals include benzyl,

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phenethyl, dibenzylmethyl, methylphenylmethyl, 3-(2-naphthyl)-butyl, and the like.

Examples of the or each carboxyl radical part of formula (III), $R_7C(O)$, $R_8C(O)$ and $R_9C(O)$, may include but are not limited to formyl, acetyl, propionyl, butyryl, pivaloyl, oxaloyl, malonyl, succinyl, glutaryl, adipoyl, benzoyl, phthaloyl, isobutyroyl, sec-butyroyl, octanoyl, isooctanoyl, nonanoyl, isononanoyl, abietyl, dehydroabietyl, dihydroabietyl, naphthenyl, anthracenyl, abietyl dimer (DYMEREX[®]), dihydroabietyl (FORAL[®]) and the like and polymers or copolymers thereof. In a preferred embodiment, said carboxyl radical parts are formyl, acetyl, propionyl or butyryl. Most preferably, the carboxyl radical part is acetyl.

The advantage of the process of the invention is that the process uses reactants which can be easily handled, are relatively inexpensive, and do not result in the emission by distillation of any harmful products. Indeed, only harmless and easily distillable acids, for example carboxylic acids, are released, thus allowing for the degree of conversion of the starting materials to the target products to be monitored by conventional analytical tools and/or by determining the amount of distilled carboxylic acid released. A further advantage is that the formed acid(s), e.g. carboxylic acids, may be removed, preferably, under distillation, preferably azeotropic distillation. A yet further advantage is that the reaction proceeds either with or without a solvent present. Moreover, the process proceeds at an acceptable rate without the need for any added catalyst. Overall, due to the simplicity and shortness, its easy work-up

procedure and its high yield, the process of the present invention can be considered as a significant and substantial improvement over the existing methods. In addition, the claimed synthesis route can be carried out at high temperatures and is therefore quick and efficient.

As noted above, the polymers formed by the process of the invention have a broad range of applications wherever there is the need for hydrolysable poly(silyl ester)s groups. The polymers thus formed exhibit a variable but predictable degradation behaviour and as such, have many potential applications. Such applications include antifouling coating applications. A further application is in the controlled release of substances, for example volatile compounds such as perfumes, fragrances or insecticides. This may be achieved by employing a resin prepared according to the invention and the volatile compound may be blended or grafted thereto. Degradable polymers have previously been used in the medical and environmental fields in view of the fact they can be synthesised with the requisite physical and mechanical properties to firstly perform a given function and then break down into biologically or environmentally resorbable small-molecule byproducts. In the medical field, the nature of the side-group on degradable polymers can create functional materials having the ability to bind to specific sites, and so on.

There are a number of applications in which a foreign body such as a metal or plastics device is implanted in a human or animal body, particularly a human body as part of a treatment. For example, broken bones may be pinned or worn out joints replaced with artificial joints.

It is desirable when metal or plastics devices are to be implanted in the body to provide such devices with a means of reducing the potential for infection or other complications. Complications associated with the use of implants include initiation of a foreign body response resulting in inflammation and fibrous encapsulation and initiation of a wound healing response resulting in hyperplasia and restenosis, as well as of course the increased risk of infection. Such complications must be addressed when introducing an implant into the body.

For example, it is desirable to provide implant devices with a means for releasing a bioactive compound in their vicinity once implanted. Some such devices are known and may for example release antibiotics to minimise the possibility of infection. Alternatively, or additionally, anti-proliferative drugs may be released to inhibit hyperplasia.

An implant device may be provided with a means for releasing a bioactive compound by applying a coating composition comprising a bioactive agent and polymers. There is a continuing need for alternative and improved coating compositions for use with implant devices.

Therefore, according to a second aspect of the present invention, there is provided a coating or film composition comprising a poly(silyl ester) as prepared or obtainable by the process hereinbefore defined.

Suitably, the coating or film composition comprises an antifouling coating composition.

The coating or film composition may comprise a coating composition suitable for use in medical and/or veterinary applications. The coating compositions may comprise a
5 coating composition for implantable medical and/or veterinary devices. The coating composition may be arranged to provide controlled release of an active agent, preferably a bioactive agent, in an aqueous system, for example a human or animal body.

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The coating composition may comprise an active agent. The active agent may comprise a bioactive agent. The bioactive agent may comprise an antibiotic and/or an anti-proliferative.

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The bioactive (e.g. pharmaceutical) agents useful in the present invention include virtually any therapeutic substance which possesses desirable therapeutic characteristics for application to the implant site.

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These agents include: thrombin inhibitors, antithrombogenic agents, thrombolytic agents, fibrinolytic agents, vasospasm inhibitors, calcium channel blockers, vasodilators, antihypertensive agents, antimicrobial agents, calcium channel blockers, vasodilators,
25 antihypertensive agents, antimicrobial agents, antibiotics, inhibitors of surface glycoprotein receptors, antiplatelet agents, antimitotics, microtubule inhibitors, antisecretory agents, actin inhibitors, remodelling inhibitors, antisense nucleotides, anti metabolites,
30 antiproliferatives (including antiangiogenesis agents), anticancer chemotherapeutic agents, anti-inflammatory steroid or non-steroidal anti-inflammatory agents, immunosuppressive agents, growth hormone antagonists,

growth factors, dopamine agonists, radiotherapeutic agents, peptides, proteins, enzymes, extracellular matrix components, ACE inhibitors, free radical scavengers, chelators, antioxidants, anti polymerases, antiviral agents, photodynamic therapy agents, and gene therapy agents.

According to a third aspect of the present invention there is provided a film or coating comprising a poly(silyl ester) as prepared or obtainable by the process hereinbefore defined.

Moreover, and according to a fourth aspect of the present invention, there is provided a poly(silyl ester) as prepared by the process hereinbefore defined.

According to a fifth aspect of the present invention there is provided an implantable medical and/or veterinary device having a coating comprising a coating or film composition comprising a poly(silyl ester) as prepared by the process hereinbefore described.

Suitably, the coating is arranged to provide controlled release of an active agent, preferably a bioactive agent, in an aqueous system.

Suitably, the device comprises an implantable medical device.

Finally, certain of the poly(silyl ester)s hereinbefore disclosed are themselves novel and form a further aspect of the present invention.

Thus, according to a sixth aspect of the present invention, there is provided a poly(silyl ester) compound comprising the repeating group of general formula (I) hereinbefore defined, and wherein L is a polylactic acid or substituted polylactic acid residue or a rosin or substituted rosin residue of a polycarboxylic acid.

According to a seventh aspect of the present invention there is provided a coating or film composition comprising a poly(silyl ester) compound comprising the repeating group of general formula (I) hereinbefore defined, and wherein L is a polylactic acid or substituted polylactic acid residue or a rosin or substituted rosin residue of a polycarboxylic acid.

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According to an eighth aspect of the present invention there is provided a film or coating comprising a poly(silyl ester) compound comprising the repeating group of general formula (I) hereinbefore defined, and wherein L is a polylactic acid or substituted polylactic acid residue or a rosin or substituted rosin residue of a polycarboxylic acid.

According to a ninth aspect of the present invention there is provided an implantable medical and/or veterinary device having a coating comprising a coating or film composition according to the seventh aspect.

The second, third, fourth, fifth and sixth aspects of the present invention may incorporate any one or more of the preferred features of the first aspect of the invention except where such features are mutually exclusive.

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The seventh aspect of the present invention may incorporate any one or more of the preferred features of the second aspect of the invention except where such features are mutually exclusive. The eighth aspect of the present invention may incorporate any one or more of the preferred features of the third aspect of the invention except where such features are mutually exclusive. The ninth aspect of the present invention may incorporate any one or more of the preferred features of the fifth aspect of the invention except where such features are mutually exclusive.

The invention will now be described by way of illustration only and with reference to the accompanying non-limiting examples and attached drawings.

Examples and Comparative Examples

Preparative Example 1

20

1,3-diacetoxytetraaisopropyldisiloxane was prepared in an analogous manner to that method disclosed by Volkova et al (see, Bull.Acad.Sci. USSR Div.Chem.Sci. (1963) 1829). Specifically, 250g of 1,3-dichlorotetraaisopropyldisiloxane (CAS No. 69304-37-6) and 282.9g of acetic anhydride were heated to about 138-146°C, whilst acetyl chloride was gently distilled off. Vacuum distillation furnished unreacted acetic anhydride and 266.2g of 1,3-diacetoxytetraaisopropyldisiloxane (106°C, 0.6 mbar, 73%) as a colourless liquid.

30

IR (film) : 2951, 2873, 1731, 1466, 1371, 1261, 1244, 1099, 1018, 937, 886, 747, 695 cm⁻¹.

NMR data have been determined in CDCl_3 and are expressed as delta versus TMS.

5 ^{13}C NMR : 170.3, 22.2, 16.8, 13.0; ^{29}Si NMR: -11.8.

Example 1

40g of 1,3-diacetoxytetraisopropyldisiloxane, prepared as
10 described in the Preparative Example above, and 16.06g of
adipic acid were heated at about 145-180°C, whilst acetic
acid was distilled out of the reactor over 6 hrs. A
polymer with a solid content of 96.1%, a molecular weight
of 4000 D (4 kD) and a viscosity of 80 dPa.s was obtained.
15 The molecular weight decrease of a THF solution was
monitored by GPC, as shown in Figure 1 of the attached
drawings.

NMR data have been determined in CDCl_3 and are expressed
20 as delta versus TMS.

^{13}C NMR : 172.8, 35.6, 24.7, 17.0, 13.1; ^{29}Si NMR : -11.38.

Comparative Example 1 (according to Wooley et al,
25 Macromolecules (1998) 31 15)

1.1325g of bis(trimethylsilyl)adipate was reacted with
1.0318g of 1,1,3,3-tetraisopropyldisiloxane at 135°C for
14 days to produce poly(tetraisopropyldisilyl oxyl
30 adipate) with a molecular weight of 2700.

Example 2

263g of FORAL[®] AX-E (dihydroabietic acid) and 308g of DYMEREX[®] (rosin dimer) were placed in a 1.2 litre flask equipped with a mechanical stirrer, a temperature control and small column with cooler and receiver. The mixture
5 was melted by heating up to 220°C. Then 120g of ethylsilyltriacetate was added and distillation of acetic acid began at 155°C and ended at 175°C. The distillation was continued under a reduced pressure of 150 mbar for 1 hour. 92g of acetic acid was distilled off, representing
10 100% of the acid that can be generated. The remaining resin was dissolved with 400g of xylene and then cooled to ambient temperature. The solid content of the product was 60%.

15 The binder solution had a viscosity of 1 dPa.s at a solid content of 60%. A drawdown of the resin solution on a glass plate showed the next day a dry/clear film. The binder film developed a light haze upon immersion in water for 24 hours, but otherwise, did not show any significant
20 changes with time. The film was then exposed to an alkaline solution of NaOH (pH value of 12.3) and exhibited hydrolysis and erosion at the surface, dissolving completely within one hour.

25 Preparative Example 2

1019.3g of adipic acid, 581.6g of neopentylglycol and 0.56g of butylstannoic acid were heated at 150-230°C whilst water distilled out of the reaction vessel. Xylene
30 was then added and the last traces of water were removed by azeotropic distillation. This gave a polyester resin at 76.5% solids with an acid value of 91.9mg KOH/g.

Example 3

423.5g of the polyester prepared as in preparative example 2, 42.3g of benzoic acid and 81.2g of ethyltriacetoxysilane were heated at 155-175°C, whilst acetic acid distilled out of the reactor, over a 4 hour period. Final dilution with xylene furnished a polymer at 84% solids. A drawdown of the resin solution on a glass plate showed the next day a dry/clear film. The film was exposed to an alkaline solution of NaOH (pH value of 12.3) and slowly dissolved.

Preparative Example 3

34.2g of L-Lactide (L-Lactic acid dimer) and 1.14g of glycolic acid were melted at 110°C. A solution of 121mg of tin di-octoate in 1 ml of toluene was then added. Polymerisation was then performed at a temperature of 110°C for 3 hours. 1.5g of succinic anhydride was then added to the polymer. After one hour at 110°C, the volatiles were stripped out of the reactor under vacuum. This gave a polymer, which had an acid value of 1.18mg KOH/g.

25 Example 4

36.8g of the polymer prepared as in preparative example 3 was heated at 100°C. 7.61g of 1,3-diacetoxytetraisopropyldisiloxane, prepared as described in the Preparative Example 1 above, was then added whilst acetic acid was distilled out of the reactor over 2 hours at a pressure of around 5 Torr. A polymer of a molecular weight of 6000 D was obtained. The molecular

weight (MW) decrease of a THF solution was monitored by GPC. The MW was 4000 D after 96 hours at room temperature. A drawdown of the resin on a glass plate showed the next day a dry/clear film. The film was
5 exposed to an alkaline solution of NaOH (pH value of 12.3) and slowly dissolved.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to
10 this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

15 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features
20 and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same,
25 equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

30 The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any

accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.